

Thermodynamics of materials

20. Chemical potentials of Atomic Defects III

Kunok Chang
kunok.chang@khu.ac.kr

Kyung Hee University

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- 1 Chemical Potentials of Atomic Defects
 - Chemical Potential of Schottky Defects
 - Chemical Potentials of Neutral Dopants
 - Chemical Potentials of Holes and Electrons

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Chemical Potential of Schottky Defects

- The creation of a Schottky defect can be expressed as



where A_A^{AB} represents an A atom occupying on the A sublattice of compound AB, and other notations are used in consistent ways.

- At equilibrium,

$$\mu_A^{AB} + \mu_B^{AB} = \mu_{V_A^{AB}} + \mu_{V_B^{AB}} + \mu_{AB}^{\circ}$$

Chemical Potential of Schottky Defects

- In the dilute solution approximation,

$$\mu_A^{AB} = \mu_A^{AB,\circ} + k_B T \ln \left(\frac{N_A - n_{V_A}^{AB}}{N_A} \right)$$

$$\mu_B^{AB} = \mu_B^{AB,\circ} + k_B T \ln \left(\frac{N_B - n_{V_B}^{AB}}{N_B} \right)$$

$$\mu_{V_A}^{AB} = \mu_{V_A}^{\circ AB} + k_B T \ln \left(\frac{n_{V_A}^{AB}}{N_A} \right) = \mu_{V_A}^{\circ AB} + k_B T \ln \left(x_{V_A}^{AB} \right)$$

$$\mu_{V_B}^{AB} = \mu_{V_B}^{\circ AB} + k_B T \ln \left(\frac{n_{V_B}^{AB}}{N_B} \right) = \mu_{V_B}^{\circ AB} + k_B T \ln \left(x_{V_B}^{AB} \right)$$



Chemical Potential of Schottky Defects

- Since the chemical potential of a compound is the sum of the chemical potentials for each component, i.e.,

$$\mu_A^{AB,\circ} + \mu_B^{AB,\circ} = \mu_{AB}^{\circ}$$

we have

$$x_{V_A^{AB}} x_{V_B^{AB}} = \exp \left[- \frac{\mu_{V_A^{AB}}^{\circ} + \mu_{V_B^{AB}}^{\circ}}{k_B T} \right] = \exp \left[- \frac{\mu_S^{\circ}}{k_B T} \right]$$

where μ_S° is the chemical potential of a Schottky defect.



Chemical Potential of Schottky Defects

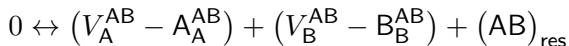
- If

$$x_{V_A^{AB}} = x_{V_B^{AB}}$$

then

$$x_{V_A^{AB}} = x_{V_B^{AB}} = \exp \left[- \frac{\mu_S^\circ}{2k_B T} \right]$$

- In Schottky notation using building elements,



where $(AB)_{\text{res}}$ represents a molecule of AB compound from a chemical reservoir of compound AB.



Chemical Potentials of Neutral Dopants

- The chemical potential of neutral dopants, μ_d° is

$$\mu_{d^\times} = \mu_d^\circ + \Delta\mu_d^\circ + k_B T \ln \left(\frac{N_{d^\times}}{N_L} \right)$$

where μ_d° is chemical potential of pure dopant d at temperature T and ambient pressure, and N_L is the total number of host lattice sites.

- The formation energy $\Delta\mu_d^\circ$ of dopant d in a host includes the formation energy and it does not include configurational entropy configuration. With quantity

$$x_{d^\times} = \frac{N_{d^\times}}{N_L}$$

we have

$$\mu_{d^\times} - \mu_d^\circ = \Delta\mu_d^\circ + k_B T \ln x_{d^\times}$$



- The solubility limit $x_{d^{\circ}}^{\circ}$ of d in host is given by

$$0 = \Delta\mu_d^{\circ} + k_B T \ln x_{d^{\circ}}^{\circ}$$

Chemical Potentials of Holes and Electrons

- For n -type semiconductor, N_c is the effective electron density of states at the conduction band edge and N_d is the number of electron donors per unit volume.
- For p -type semiconductor, N_v is the effective hole density of states at the valence band edge and N_a is the number of electron acceptors per unit volume.
- The chemical potentials of electrons and holes without electric field is

$$\mu_e = E_c + k_B T \ln \left(\frac{n}{N_c} \right) \simeq E_c + k_B T \ln \left(\frac{N_d}{N_c} \right)$$

$$\mu_h = -E_v + k_B T \ln \left(\frac{p}{N_v} \right) \simeq -E_v + k_B T \ln \left(\frac{N_a}{N_v} \right)$$



Chemical Potentials of Holes and Electrons

- For $p - n$ junctions, the electric field presents at the junction region, the electric field at n -type semiconductor ϕ^n and the field in p -type semiconductor is ϕ^p ,

$$\tilde{\mu}_e = E_c - e\phi^n + k_B T \ln \left(\frac{N_d}{N_c} \right)$$

and

$$\tilde{\mu}_h = -E_v + e\phi^p + k_B T \ln \left(\frac{N_a}{N_v} \right)$$

Chemical Potentials of Holes and Electrons

- At equilibrium,

$$0 = \tilde{\mu}_e + \tilde{\mu}_h$$

therefore,

$$0 = E_c - e\phi^n + k_B T \ln \left(\frac{N_d}{N_c} \right) - E_v + e\phi^p + k_B T \ln \left(\frac{N_a}{N_v} \right)$$

proceed to

$$\Delta\phi = \phi^n - \phi^p = \frac{E_g}{e} + \frac{k_B T}{e} \ln \left(\frac{N_d N_a}{N_c N_v} \right) = \frac{k_B T}{e} \ln \left(\frac{N_d N_a}{n_i^2} \right)$$

where

$$E_g = E_c - E_v$$

the band gap energy and n_i is the intrinsic concentration of electrons and holes without dopants,

$$n_i^2 = N_c N_v \exp \left(- \frac{E_g}{k_B T} \right)$$

